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14. ABSTRACT
The purpose of this work was to investigate the possibility of utilizing metalloporphyrins as the catalysts for aerobic oxidation of alcohols. We proposed to investigate the catalytic activity of the metalloporphyrins in solution and in a polymer-supported form. The porous polymer was anticipated to concentrate substrates, especially in the inflammable fluorinated solvents. Since oxygen solubility in fluorinated solvent is several times higher than in nonfluorous organic solvents, such systems were expected to be good media for aerobic oxidations.

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Combination Sorbent And Reactive Chemistries For Use In Highly Efficient Aerobic Oxidations (W911NF0510081)

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Statement of Problem Solved

The purpose of this work was to investigate the possibility of utilizing metalloporphyrins as the catalysts for aerobic oxidation of alcohols. We proposed to investigate the catalytic activity of the metalloporphyrins in solution and in a polymer-supported form. The porous polymer was anticipated to concentrate substrates, especially in the inflammable fluorinated solvents. Since oxygen solubility in fluorinated solvent is several times higher than in nonfluorous organic solvents,[1] such systems were expected to be good media for aerobic oxidations.

To this end we investigated the catalytic activity of a variety of metalloporphyrin complexes. These compounds were synthesized from metal salts and free porphyrin ligands, and then were derivatized for the preparation of polymer-supported catalysts. We tested their performance under a broad set of reaction conditions, including the screening of a number of activating additives. We summarize the details of these studies below.

Summary

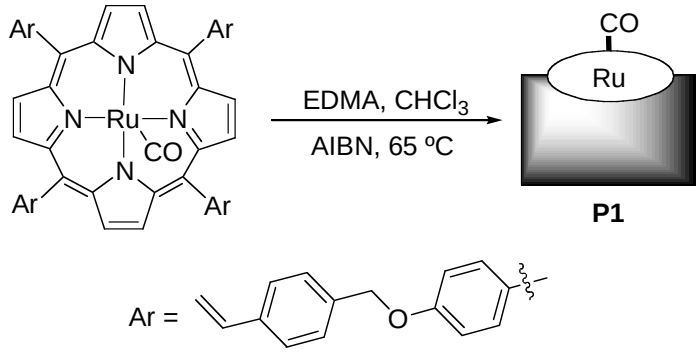
In this report we present the results from our development of new catalytic systems for the aerobic oxidation of alcohols to ketones. The oxidation of alcohols to carbonyl compounds is a common and important transformation in organic synthesis. Although there are many different methods for such functional group manipulations, environmentally friendly and atom efficient catalytic aerobic procedures are in high demand. The use of molecular oxygen as a stoichiometric oxidant is very attractive since innocuous byproducts result (H_2O or H_2O_2).[2] Modern, metal catalyzed aerobic oxidation of alcohols have recently been reviewed[3,4] and these collections outline significant progress in the elaboration of homogeneous and/or heterogeneous ruthenium catalysts.[5,6] Since Groves' pioneering discovery of the aerobic epoxidation of olefins catalyzed by the cytochrome P450 analog dioxo(tetramesitylporphyrinato)ruthenium,[7] numerous investigations have focused on aerobic and anaerobic oxidative transformations catalyzed by ruthenium porphyrin complexes.[8] Although Hirobe[9] and Groves[10] have reported high turnover numbers (TON) using 2,6-disubstituted pyridine-*N*-oxides as

the stoichiometric oxidants, similarly affective aerobic oxidation of alcohols remain largely unreported.[11]

1st Generation Ruthenium-Porphyrin Complex

We in collaboration with Prof. Severin (EPFL-Lausanne, Switzerland) recently prepared an immobilized Ru(*meso*-tetraarylporphyrin) complex **P1** (Scheme 1) and investigated its catalytic activity in the epoxidation of olefins and oxidation of alcohols and alkanes using 2,6-dichloropyridine-*N*-oxide as a stoichiometric oxidant.[12] Our group recently noted a "fluorophobic" effect that increased the local concentration of organic compounds within the interior of monolithic organic polymers.[13] Concentration enhancements within the volume of the polymer particles of up to 180-fold were documented. This phenomenon led to improvements in the rate of polymer immobilized catalysts and solid-phase reactions in the fluorous systems.[14,15]

Scheme 1



EDMA = ethylene glycol dimethacrylate

We also sought to utilize catalyst **P1** to mediate oxidation of benzhydrol Ph_2CHOH using molecular oxygen as a model reaction for the oxidative destruction for a putative stimulant molecule. Methylnonafluorobutyl ether $C_4F_9OCH_3$ (HFE-7100) was used as the solvent for the fluorophobic acceleration of the oxidation. We determined the partition efficiency for the distribution of benzhydrol and the product of oxidation – benzophenone $Ph_2C=O$ - between the solvent and the polymer surface (Table 1). These data demonstrated that substrate adsorption on the polymer surface indeed occurs and that differences in reactant structures leads to significant differences in the partition efficiency.

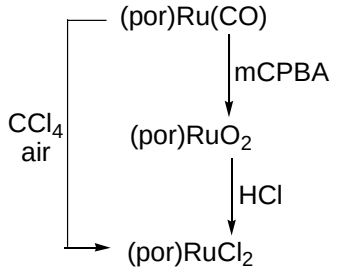
Table 1. Partition efficiency

Compound	Temperature	PE[a]
Ph_2CHOH	26 °C	254
Ph_2CHOH	55 °C	83
$Ph_2C=O$	26 °C	79
$Ph_2C=O$	55 °C	26

[a] partition efficiency is the equilibrium concentration of the analyte in the polymer phase divided by the initial solution concentration. This value best reflects the enhancements in local concentration that occur upon the addition of polymer.

The catalytic activity of **P1** was examined for the aerobic oxidation of benzhydrol to benzophenone under an O_2 atmosphere (1 atm), the conversion was monitored by ^1H NMR or gas chromatography of the reaction mixture (Table 2). Complex **P1** itself was inactive at rt and 50 °C (entry 1). We hypothesized that the catalyst needed to be activated, perhaps by first transforming ruthenium-carbonyl to a more oxidized form. Hirobe[9] and later Iida[16] reported that the mineral acids HCl and HBr could be used to enhance the activity of ruthenium porphyrin complexes, presumably by forming more active halo-ruthenium porphyrin complexes. Dihalogen ruthenium porphyrins can also be prepared from carbonyl ruthenium precursors by reaction with CCl_4 or CBr_4.[17,18] (Scheme 2). In addition, an oxidation of ruthenium carbonyl complexes with mCPBA converted them to dioxo complexes.[17]

Scheme 2

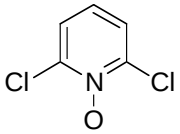


mCPBA - *meta*-chloroperbenzoic acid

With these early results in mind, we examined a wide range of the additives for the enhancement of the catalyst performance (Table 2). However, standard oxygen-transfer reagents, such as mCPBA and pyridine-*N*-oxide, didn't improve the activity of the catalyst. Carrying out oxidations in a 9:1 mixture of HFE-7100 and bromotrichloromethane (function both as a co-solvent and activator), increased the conversion of benzhydrol to 5 % (Entry 7); further replacement of all fluorous solvent to $CBrCl_3$ resulted in increasing of the conversion to 11 % (turnover number TON = 22). These results were taken to be very promising as the TONs began to approach some of the best values reported to date. Combined activation of the catalyst with bromotrichloromethane and hydrobromic acid (Entry 9)

increased conversion to 21 % (TON = 42). Unfortunately, we then found the benzhydrol to be acid-sensitive, and the rest of starting material was decomposed by HBr. Attempts to neutralize the acid with organic bases after catalyst activation did not suppress the undesired decomposition of benzhydrol.

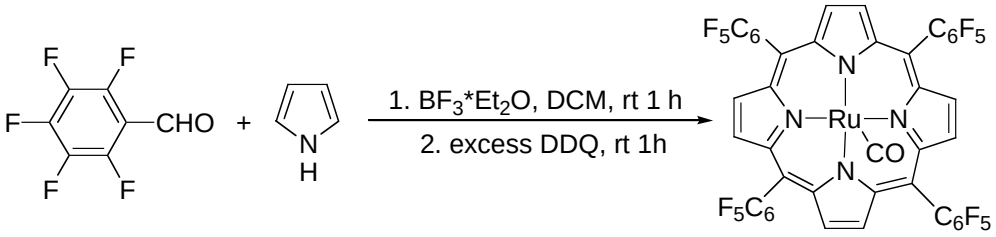
Table 2

Entry	Additive	Temperature	Conversion to $Ph_2C=O$
1	-	rt	traces
2	-	50 °C	1
3	 10 mol %	55 °C	5
4	mCPBA 10 mol %	55 °C	13
5	CCl_4	55 °C	2
6	TEMPO	55 °C	traces
7	$CBrCl_3$	55 °C	5
8	$CBrCl_3$ as a solvent	55 °C	11
9	$CBrCl_3$ – HBr aq	55 °C	21

2nd Generation Ruthenium-Porphyrin Complex

Stimulated by the high performance of ruthenium complexes in polyhalogenated porphyrins,[9,10,19] we next studied the catalytic activity of carbonylruthenium tetrakispentafluorophenylporphyrin Ru(TPFPP)(CO) **1** for the homogeneous aerobic oxidation of alcohols. The stability of these halogenated derivatives to oxidative destruction and their modified redox potentials were properties that we hoped would successfully overcome the inactivity of the 1st generation catalyst. 2nd Generation ruthenium-porphyrin complex was easily prepared from commercial reagents (Scheme 3).

Scheme 3

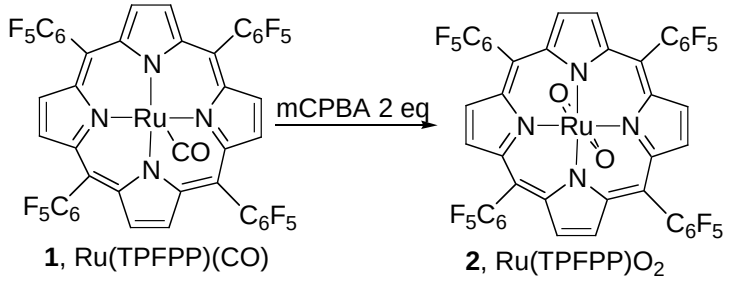


$TPFPPH_2$ 47 %

$TPFPPH_2$ + $Ru_3(CO)_{12}$ —reflux at 214 °C→ Ru(TPFPP)(CO) **1**, 76 %

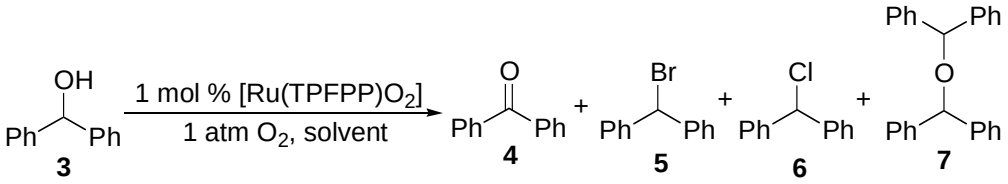
The catalytic activity of **1** was examined for the aerobic oxidation of benzhydrol **3** to benzophenone **4** in various solvents under an O_2 atmosphere (1 atm) at different temperatures (Table 3).

The conversion of **3** to **4** was monitored by ^{1}H NMR of the reaction mixture using *tert*-butylbenzene as an internal standard. Complex **1** itself was inactive at 60 °C until preoxidized to the *trans*-dioxo form **2** (Entry 1). Complex **2** was prepared *in situ* by oxidation of **1** with two equivalents of mCPBA at 60 °C and used without isolation (eq. 1).



1, Ru(TPFPP)(CO) **2**, Ru(TPFPP)O_2

Table 3



entry	catalyst	solvent/additives	temperature	time	TON to 4[a]
1	**1**	$CBrCl_3$	60 °C	18 h	4
2	**2**[b]	CCl_4	60 °C	4 h	1.5
3	**2**[b]	CD_3CN	60 °C	4 h	2
4	**2**[b]	PhCl	100 °C	4 h	4
5	**2**[b]	C_4F_9OMe-$CBrCl_3$ 9 : 1 v/v	60 °C	4 h	< 1
6	**2**[b]	$CBrCl_3$	60 °C	3 h	10
7[c]	**2**[b]	$CBrCl_3$	80 °C	22 h	31
8[c]	**2**[b]	$CBrCl_3$	100 °C	18 h	74
9[d]	**2**[b]	$CBrCl_3$–D_2O-NaOD (250 mol %)	90 °C	4 h	63
10[d]	**2**[b]	$CBrCl_3$–D_2O-NaOD (250 mol %)	100 °C	3 h	30
11	**2**[b]	$CBrCl_3$–H_2O-Bu_4NOH (25 mol %)	90 °C	24 h	99
12	**1**	$CBrCl_3$–H_2O-Bu_4NOH (25 mol %)	90 °C	24 h	96

[a] Determined by ^{1}H NMR, internal standard *t*-butylbenzene. [b] Catalyst **2** prepared *in situ* from **1.** [c] Reaction accompanied with the formation of side products **5**, **6**, **7.** [d] Reaction stopped after destruction of ruthenium porphyrin

The combination of $CBrCl_3$ and **2** is nearly inert without O_2, as demonstrated by heating **3** with $CBrCl_3$ and catalyst **2** at 100 °C under argon. Analysis after 20 h showed a 4 % conversion to benzophenone, which can be attributed to stoichiometric oxidation of **3** with dioxoruthenium complex **2**. Catalytic oxidations of **3** to **4** in $CBrCl_3$, however, were accompanied by significant amounts of the

undesirable **5**, **6** and **7**.[20] Higher temperatures accelerated the oxidation but also increased the proportion of side products. These compounds could be suppressed with an inorganic base (entries 9, 10), but at the cost of an accelerated rate of catalyst destruction. Catalyst longevity could be recovered by adding an aqueous solution of Bu_4NOH (25 mol % to **3**) to act as a phase transfer reagent and base. Under these optimum conditions the selectivity increased to 99 % (entry 11), and **1** did not even need preactivation with mCPBA to be effective (entry 12).

As shown in Figure 1, the progression of the oxidation was investigated at different loadings of catalyst **2**. In each case an induction period was observed and a relatively constant growth of benzophenone ensued. Unexpectedly, the quickest initiation occured at a 1000:1 substrate to catalyst ratio (S/C).

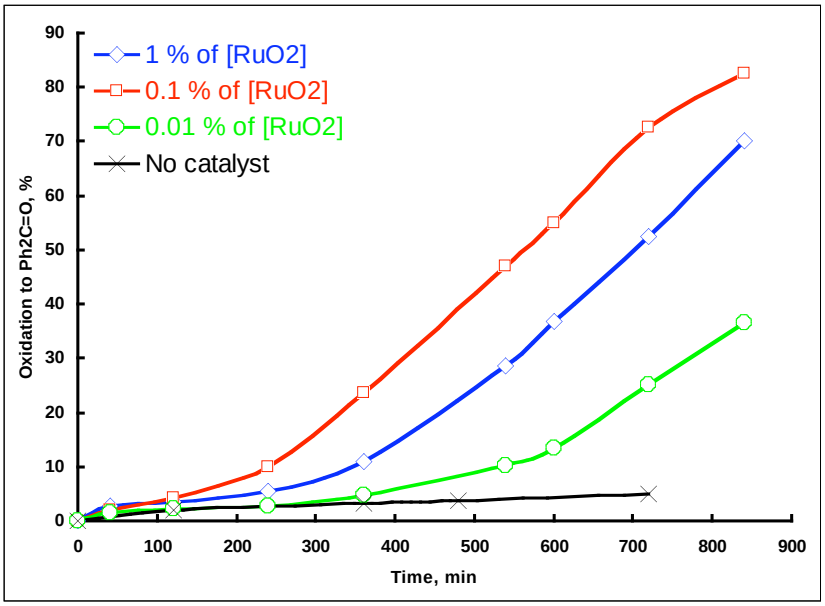


Figure 1. Catalytic vs. autooxidation of **3** with different S/C ratio (NMR monitoring)

The viability of an autooxidation process was investigated by similarly following the reaction in the absence of catalyst. In this manner it was established that over the first 24 h period, the autooxidation was much slower (6 % conversion) than with ruthenium (Figure 1, entry 1 in Table 4). When this same reaction was quantified after 65 h, however, complete oxidation had occurred (entry 1). The autocatalytic nature of this oxidation was traced to a benzophenone-mediated photo-autooxidation under normal hood light (entry 2). It was additionally established that the autooxidation was almost completely suppressed (7 % conversion at 48 h) in the dark even with added benzophenone (entry 3). Repeating catalytic reactions under the optimum conditions, but wrapped in foil, indicated that the ruthenium-mediated oxidation was insensitive to light (entries 4, 5). It was also found that BHT (2,6-di-*tert*-butyl-4-methylphenol) effectively terminated the autooxidation pathway (entry 6), while it only slightly inhibited the ruthenium-catalyzed oxidation (Entry 7). The outcome of these experiments were thus consistent with a scenario wherein ruthenium-catalyzed oxidation occurs, in parallel and perhaps independent to a radical chain autooxidation,

that is silent in the dark or with a radical trap. Conditions could be engineered to exclude the autooxidation pathway but under typical conditions it seems, at least for the photosensitizer benzophenone, that both pathways occur to some degree.

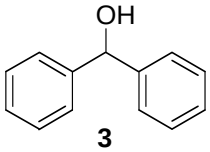
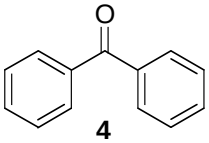
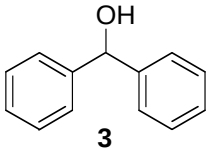
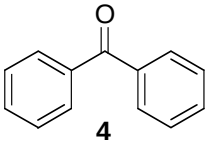
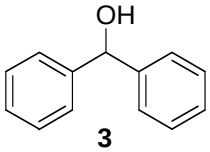
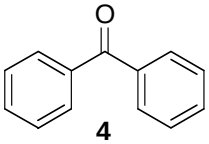
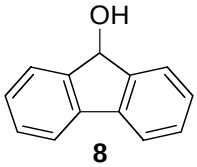
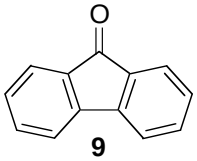
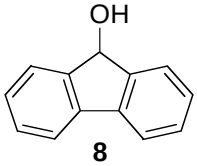
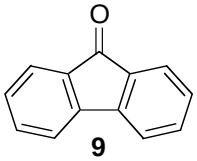
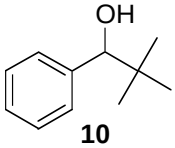
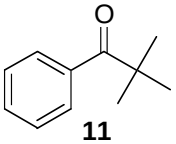
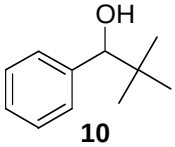
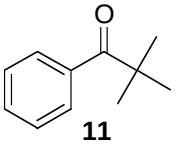
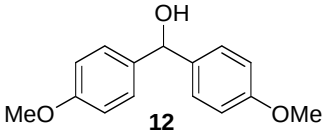
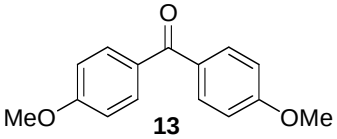
Table 4. Control experiments

entry	catalyst	conditions[a]	time	TON to 4[b]
1	No cat	-	24 h	6
			65 h	99
2	No cat	+ 25 mol % Ph_2CO	12 h	100
3	No cat	+ 25 mol % Ph_2CO dark	48 h	7
4	**2**[c,d]	-	20 h	92
5	**2**[c,d]	dark	24 h	82
6	No cat	+ 10 mol % BHT	72 h	NR
7	**2**[c]	+ 10 mol % BHT	24 h	61

[a] All reactions were performed with the standard conditions (0.2 mmol of **3**, 10 mL of $CBrCl_3$, 0.05 mL of 1 M aqueous solution of Bu_4NOH) system at 90 °C. [b] Determined by ^1H NMR, internal standard *t*-butylbenzene. [c] Catalyst **2** prepared *in situ* from **1.** [d] S/C = 10000

This optimized catalytic system was used in the oxidation of a set of secondary alcohols (Table 5). To evaluate the maximal turnover number (TON), experiments with decreasing catalyst concentration (higher substrate to catalyst ratio, S/C) were carried out. With a S/C ratio of 10,000 a TON 8200 was achieved for benzhydrol **3**; even higher turnovers were observed for **8** and **10**. The corresponding ketones **4**, **9**, **11** were isolated in high yields. 4,4′-Dimethoxybenzhydrol **12** was also oxidized to the ketone **13** in good yield, however oxidation was complicated by the formation of unidentified side products. Oxidation of other alcohols – 1-phenylethanol and benzyl alcohol – resulted in the formation of multiple products.

Table 5. Oxidation of various alcohols catalyzed by ruthenium porphyrin after 24 h[a]

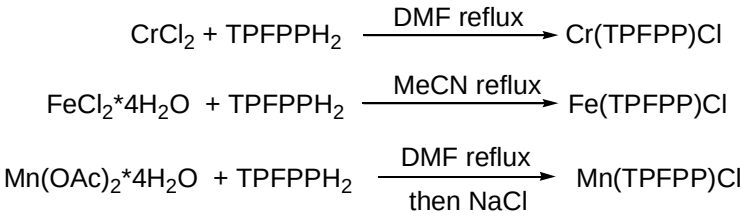
entry	substrate	S/C	ketone, %[b] (yield)	TON	product
1	 **3**	100	95	95	 **4**
2	 **3**	1000	99 (97)	990	 **4**
3	 **3**	10000	82	8200	 **4**
4	 **8**	1000	95 (92)	950	 **9**
5	 **8**	10000	99	9900	 **9**
6	 **10**	1000	99 (98)	990	 **11**
7	 **10**	10000	99	9900	 **11**
8	 **12**	1000	77 (73)	770	 **13**

[a] see Experimental Section. [b] Determined by ^{1}H NMR, internal standard *t*-butylbenzene

Porphyrin Complexes of First Row Transition Metals

We also examined the catalytic activity of first row transition metals – chromium, manganese and iron. The corresponding complexes were prepared from metal salts and free porphyrin ligand (Scheme 4). All complexes were characterized by comparison of the UV spectra in solution with the literature data.

Scheme 4



Activity of such metalloporphyrins in the catalytic oxidation reactions was examined under 1 atm of oxygen. The following reactions were studied: a) oxidation of secondary alcohols to ketones; b) oxidation of C-H bond; c) epoxidation; d) oxidation of sulfides to sulfoxides. Unfortunately, after a wide screening of other solvents and activators, these systems didn't exhibit any catalytic activity in the aerobic oxidations.

Closing statement

A series of transition metal-porphyrin complexes (chromium, manganese, iron, ruthenium) were prepared and examined in the aerobic oxidation of alcohols under mild conditions. We found that complexes of first row metals were inactive at any conditions tested, whereas complexes of ruthenium exhibits poor to good catalytic activity. We further established that the performance of the ruthenium catalysts was determined by the nature of the porphyrin ligand.

After activating with $CBrCl_3$, a polymer-supported ruthenium-porphyrin catalyst **P1** functioned as a catalyst for the aerobic oxidation of benzhydrol to benzophenone in the fluorous solvent HFE-7100. TONs up to 10-22 were achieved. Activation of the catalyst with bromotrichloromethane and HBr together increased the turnover number to 42. Unfortunately, utilization of HBr also resulted in undesired decomposition of the acid-sensitive starting material.

More robust 2nd generation tetrakispentafluorophenylporphyrin complexes were also studied as catalysts. The combination of dioxoruthenium tetrakispentafluorophenylporphyrin Ru(TPFPP)O_2 **2** with 25 mol % Bu_4NOH in $CBrCl_3$ effectively catalyzes the oxidation of non-enolizable secondary alcohols to ketones in good to excellent yields with molecular oxygen. Control experiments indicated that under the optimum reaction conditions ruthenium catalysis and autooxidation were both viable, though conditions could be engineered (radical traps or dark) wherein the autooxidation pathway was shut down and only ruthenium-catalysis converted alcohol to ketone. Turnovers up to 9900 were documented. To the best of our knowledge, these results provide the first example of the successful aerobic oxidation of alcohols catalyzed with ruthenium porphyrin complex.

Bibliography

(1) *Handbook of Fluorous Chemistry*, Gladysz, J. A., Curran, D. P., Horvath, I. T., Eds.; Wiley-VCH: Weinheim, 2005.

(2) *Modern Oxidation Methods* (Ed.: J.-E. Bäckvall), Wiley-VCH, Weinheim, **2004**.

(3) For general reviews see a) R. A. Sheldon, I. W. C. E. Arends, *Catalytic oxidations of alcohols*, In *Advances in Catalytic Activation of Dioxygen by Metal Complexes* (Ed.: L. I. Simándi), Kluwer Academic Publishers, London, **2003**, pp. 123-155; b) I. W. C. E. Arends, R. A. Sheldon, *Modern Oxidation of Alcohols Using Environmentally Benign Oxidants*, In [1], pp. 83-118; c) I. E. Markó, P. R. Giles, M. Tsukazaki, A. Gautier, R. Dumeunier, K. Doda, F. Philippart, I. Chellé-Regnault, J.-L. Mutonkole, S. M. Brown, C. J. Urch, *Aerobic, Metal-Catalyzed Oxidation of Alcohols*, In *Transition Metals for Organic Synthesis*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**, pp. 437-478; d) B.-Z. Zhan, A. Thompson, *Tetrahedron* **2004**, *60*, 2917-2935; e) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037-3058; f) M. J. Schultz, M. S. Sigman, *Tetrahedron* **2006**, *62*, 8227-8241.

(4) For Ru-catalyzed aerobic oxidations see: a) B. R. James, *Selective oxidations with dioxygen catalyzed by ruthenium and rhodium complexes*, In *Dioxygen Activation and Homogeneous Catalytic Oxidation* (Ed.: L. I. Simándi), Elsevier, Amsterdam, **1991**, pp. 195-212; b) T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599-2660; c) M. Pagliaro, S. Campestrini, R. Ciriminna, *Chem. Soc. Rev*. **2005**, *34*, 837-845.

(5) a) I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnault, C. J. Urch, S. M. Brown, *J. Am. Chem. Soc*. **1997**, *119*, 12661-12662; b) N. Komiya, T. Nakae, H. Sato, T. Naota, *Chem. Comm*. **2006**, 4829-4831; c) F. Shi, M. K. Tse, M. Beller, *Chem. Asian J*. **2007**, *2*, 411-415.

(6) For the application of heterogeneous ruthenium catalysts in aerobic oxidation of alcohols see: a) K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed*. **2002**, *41*, 4538-4542; b) K. Yamaguchi, N. Mizuno, *Chem. Eur. J*. **2003**, *9*, 4353-4361; c) H.-Y. Shen, S.-C. Zhou, M.-H. Wei, H.-X. Zong, *React. Funct. Polymers* **2006**, *66*, 827-831; d) T. Matsumoto, M. Ueno, J. Kobayashi, H. Miyamura, Y. Mori, S. Kobayashi, *Adv. Synth. Catal.* **2007**, *349*, 531-534;

(7) J. T. Groves, R. Quinn *J. Am. Chem. Soc.* **1985,** *107***,** 5790-5792

(8) For the reviews of oxidations catalyzed by ruthenium porphyrin complexes, see: a) B. Meunier, *Chem. Rev*. **1992**, *92*, 1411-1456; b) T. Mlodnicka, B. R. James, *Oxidations Catalyzed by Ruthenium Porphyrins*, In *Metalloporphyrins Catalyzed Oxidations* (Eds.: F. Montanari, L. Casella), Kluwer Academic Publishers, London, **1994**, pp. 121-148; c) J. T. Groves, K. Shalyaev, J. Lee, *Oxometalloporphyrins in Oxidative Catalysis*, In *The Porphyrin Handbook*, Vol. 4 (Eds.: K. Kadish, K.

Smith, R. Guilard), Academic Press, New York, **2000**, pp. 17-40; d) M. B. Ezhova, B. R. James, *Catalytic oxidation using ruthenium porphyrins*, In *Advances in Catalytic Activation of Dioxygen by Metal Complexes* (Ed.: L. I. Simándi), Kluwer Academic Publishers, London, **2003**, pp. 1-77.

(9) a) T. Higuchi, H. Ohtake, M. Hirobe, *Tetrahedron Lett*. **1989**, *30*, 6545-6548; b) T. Higuchi, H. Ohtake, M. Hirobe, *Tetrahedron Lett*. **1991**, *32*, 7435-7438; c) H. Ohtake, T. Higuchi, M. Hirobe, *J. Am. Chem. Soc*. **1992,** *114*, 10660-10662; d) H. Ohtake, T. Higuchi, M. Hirobe, *Tetrahedron Lett*. **1992**, *33*, 2521-2524; e) H. Ohtake, T. Higuchi, M. Hirobe, *Heterocycles* **1995**, *40*, 867-903; f) T. Higuchi, M. Hirobe, *J. Mol. Catal. A*, **1996**, *113*, 403-422.

(10) a) J. T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, *J. Am. Chem. Soc*. **1996,** *118*, 8961-8962; b) C. Wang, K. V. Shalyaev, M. Bonchio, T. Carofiglio, J. T. Groves, *Inorg. Chem*. **2006**, *45*, 4769-4782.

(11) TONs of about 1.5/day are realized for oxidation of isopropanol: S. Y. S. Cheng, N. Rajapakse, S. J. Rettig, B. R. James, *Chem. Comm*., **1994**, 2669-2670.

(12) a) O. Nestler, K. Severin, *Org. Lett.* **2001**, *3*, 3907-3909; b) E. Burri, M. Öhm, C. Daguenet, K. Severin *Chem. Eur. J*. **2005**, *11*, 5055 – 5061; c) E. Burri, S. M. Leader, K. Severin, M. R. Gagné, *Adv. Synth. Cat*. **2006**, *348*, 1640-1644; d) E. Burri, K. Severin, *Chimia* **2006**, *60*, 182-184.

(13) Leeder, S. M.; Gagné, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 9048.

(14) Vinson, S. M.; Gagné, M. R. *Chem. Comm.* **2001**, 1130.

(15) Morphy, J. R.; Rankovic, Z.; York, M. *Tetrahedron Lett*. **2001**, *42*, 7509.

(16) S. Ogawa, T. Iida, T. Goto, N. Mano, J. Goto, T. Nambara, *Org. Biomol. Chem*. **2004**, *2*, 1013-1018.

(17) C. Wang, K. V. Shalyaev, M. Bonchio, T. Carofiglio, J. T. Groves, *Inorg. Chem*. **2006**, *45*, 4769-4782.

(18) Z. Gross, C. M. Barzilay, *Chem. Comm*. **1995**, 1287-1288.

(19) a) S.-I. Murahashi, T. Naota, N. Komiya, *Tetrahedron Lett*. **1995**, *36*, 8059-8062; b) E. R. Birnbaum, J. A. Labinger, J. E. Bercaw, H. B. Gray, *Inorg. Chim. Acta* **1998**, *270*, 433-439.

(20) Identity of compounds **5-7** was established by the comparison of their 1H NMR spectra with literature data: a) L. J. Stangeland, J. Songstad, *Acta Chem. Scand*. **1970**, *24*, 356-358; b) K. J. Miller, M. M. Abu-Omar, *Eur. J. Org. Chem*., **2003**, 1294-1299.